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THERMOSTABLE SOLUBLE POLYIMIDES

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ABSTRACT. A new method is developed for synthesizing high-
molecular aromatic polyimides -- single-stage high-temperature
polycyclization in solution -- which considerably simplifies
the synthesis and use of such polymers. An idea of the molec-
ular structure and coefficient of polydispersity of the
polyimides is obtained for the first time on the basis of
polydiphenylene-phthalide pyromellitimide as an example.
Some physicochemical properties of anilinephthalein imide
and anilinephthalein polyimides are studied, and it is found
that these polymers have a valuable set of properties: high
mechanical indices and exceptional thermal stability, which,
when combined with the excellent solubility of the given
polyimides, make them extremely promising for practical use.
The problem of the effect which various structural factors
have on the solubility of the polyimides is discussed, and
it is shown that the solubility of anilinephthalein imide
and anilinephthalein polyimides is due to the large size and
the polarity of the phthalide and phthalimidine side groups.

The valuable physicochemical properties of aromatic polyimides are fairly /2267*
known at the present time [1-3]. Obviously the realization of these pro-
perties, i.e., the use of polyimides in the most varied branches of techno-
logy, is an extremely important and pressing problem. However, in many cases
the extensive practical utilization of polyimides is impeded by the necessity
for using high temperatures (300°) and a vacuum during polycyclization of poly-
amide acids directly in the finished articles, which is due to the insolubility
and infusibility of most of these acids in the cyclized form. We have produced
soluble aromatic polypyromellitimides for the first time by synthesis from
aromatic diamines containing large polar side radicals cyclically bound to the
central carbon atom (anilinephthalein and anilinephthalein imide) [4]. The
solubility of anilinephthalein polyimides has opened up extensive possibilities
for improving the method of synthesis and studying this class of polymers,
which is the subject of this article, in addition to analysis of some physico-
chemical properties of the given polymers.

Before going into a discussion of the experimental results, let us pause
for a moment to consider the part played by the structural factors**

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* Numbers in the margin indicate pagination in the foreign text.
** Here we shall be speaking of utilizing for soluble polymer synthesis only
   those structures which do not reduce, but rather increase the heat
   resistance of the polymers without decreasing their thermal stability.

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responsible for the solubility of many of these polymers. The phthalide and phthalimidine groups which comprise the lateral framework of soluble anilinephthalein polyimides and anilinephthalein imide have the following two special characteristics: large size and polarity. It is precisely the integral effect of both these factors which is responsible for the solubility of the aromatic polyimides. The large side radicals in the macromolecule of these polymers bring about a relaxation in the packing density of the polymer chains.

However this factor alone, although it is extremely important, is not enough in itself to make polymers insoluble, particularly when we are dealing with such rigid-chain polymers as aromatic polypyromellitimides. This becomes obvious when consideration is given to the fact that high-molecular polypyromellitimides with large fluorene side radicals (based on *9,9-bis*-[4-aminophenyl] fluorene), like most other polyimides, are insoluble in organic solvents. However, the polarity of the phthalide and phthalimidine groups apparently aids in improving the solvation of the polymer by polar solvents, which in the final analysis also leads to disintegration of the structure. Therefore the insolubility of previously described aromatic polypyromellitimides is due not to their three-dimensional structure, but rather to the rigidity of the cyclolinear structure of these polymers, and to the considerable intermolecular interaction resulting from the polar carbonyl groups of the imide ring.

In studying the chemical destruction of soluble polydiphenylenephthalide pyromellitimide, we showed [5,6] that polyimides, at least up to 200°C, go through aminolysis only. Another important result of these experiments was establishment of the fact that polyimides are depolymerized in solutions of dimethylformamide (DMFA)*, dimethylacetamide (DMAC), and dimethylsulfoxide (DMSO) and N-methylpyrrolidone, remaining stable up to 210°C in a number of other solvents. Because of the solubility of anilinephthalein polyimides and their stability at high temperatures in a number of solvents, we were able to find a fundamentally different method for synthesizing them -- single-stage high-temperature polycyclization in solution.   /2268

Actually, as is well known, the most common and successful method for synthesis of insoluble and infusible aromatic polyimides is two-stage polycyclization with the formation of a high-molecular polyamido acid in the first stage of the reaction, and cyclic depolymerization of this acid in the finished article before formation of the polyimide. In addition to the obvious advantages of this method, which may be used for producing articles with important properties from polyimides which are infusible and insoluble in most cases in the final stage, the procedure also has some inherent disadvantages such as: a) the difficulty of producing high-molecular polyimides in a block or thin film because of the intensive hydrolysis of the polyamido acid due to the water given off during cyclization; b) degradation of the polyimides by solvents (see above) which remain in the polymer even after heating at elevated temperatures; c) the necessity for using high temperatures (frequently ~300°C) and a vacuum for producing polyimide articles with satisfactory physical properties [8,9].

* There is indirect evidence that polydiphenylene oxide pyromellitimide is also unstable in the presence of DMFA at high temperatures [7].

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On the other hand, when polyimides are synthesized by high-temperature polycyclization in an enert solvent (nitrobenzene), as the aromatic diamine first begins to interact with the tetracarboxylic acid dianhydride, an amido acid is formed which precipitates since it is insoluble in this solvent. The next reaction in polymer formation (polycyclization) takes place at a temperature of 160-210°C accompanied by conversion of the insoluble oligomer amido acid to a soluble polyimide. The ~100% conversion of the polyamido acid to polyimide by this method of polycyclization is indicated by the infrared spectrum of the polyimide which displays all bands characteristic of the five-member imide ring, and absence of bands characteristic of the >NH group (amide). Therefore the difficulties associated with degradation of polyamido acids and polyimides are obviated by using this method of polymer synthesis, and besides, vacuum treatment of polyimide articles at extremely high temperatures is no longer necessary.

A comparatively long time interval is required for completing polycyclization in a nitrobenzene solution, although a polyimide of high molecular weight is formed after only 10 hours at 200°C. It should be pointed out that the molecular weight of a polymer synthesized under these conditions varies over a very extensive range depending on the concentration of the initial materials in the nitrobenzene. For instance when the concentration of the initial components is varied from 0.1 to 0.6 M/ℓ the η_{ln} of the resultant polyimide in DMFA changes from 1.0 to 2.3 dl/g. It would hardly be advisable to carry out polycyclization in more highly concentrated solutions since here there are considerable difficulties in agitating the reaction mass and removing water from the reaction zone.

An appreciable advantage of this single-stage high-temperature method of synthesizing polyimides in solution is the absence of destructive processes during polycyclization in nitrobenzene with resultant production of anilinephthalein polyimides of considerably higher molecular weight than that achieved by the now widely used two-stage method: the maximum η_{ln} of anilinephthalein polypyromellitimide synthesized by the two-stage method has been 0.55 dl/g (see Table 1 below). Another important feature is that the reaction <u>/2269</u> solution resulting from polycyclization may be used directly for making products (lacquers, fibers, binders for fiberglass plastics) without the subsequent heat treatment which is necessary in cyclization of polyamido acids. The given method has also been used for successful synthesis of polyimides which, although they are insoluble in nitrobenzene, do not precipitate out of the reaction medium during synthesis forming metastable solutions [for instance we used this method to produce 9,9-bis-(4-aminophenyl)fluorene polypyromellitimide with η_{ln} = 0.65 dl/g (H_2SO_4)], as well as insoluble, infusible polyimides which can be used for producing finished articles by conventional methods. The single-stage method of synthesis may obviously be extended to production of a number of high-molecular polyimides which are insoluble, infusible, and only swell in the reaction medium, but are soluble in other solvents (this applies specifically to the polyimides of anilinephthalein imide, which are insoluble in nitrobenzene), which makes it possible to rework them.

Valuable information on the structure of polymers may be derived from studying their behavior in solutions. The synthesis of soluble anilinephthalein pyropolymellitimide and anilinephthalein imide has given us an opportunity for the first time to determine the polydispersity and molecular weights of aromatic polyimides. We give below only the first results of these investigations. They will be considered in greater detail in a separate article.

TABLE 1. MOLECULAR WEIGHTS AND COEFFICIENT OF POLYDISPERSITY OF ANILINEPHTHALEIN POLYPYROMELLITIMIDE

Speci-men #	$[\eta]^{20°}$ in DMFA, dl/g	$\overline{M}_w$ by light scatter-ing $\times 10^{-3}$	Sedimentation $\times 10^{-3}$			$\overline{M}_z/\overline{M}_w$	Constant of sedi-menta-tion $\times 10^{13}$ $S_{0.5}$	Coefficient of diffu-sion $\times 10^{13}$, $D_{0.5}$
			$\overline{M}_{w0.5}$	$\overline{M}_{z0.5}$	$\overline{M}_w$			
			according to Archibald		according to Svedberg			
1*	0.53	20.0	20.4	45.2	17.5	2.22	1.69	0.64
2**	1.02	55.0	60.5	82.8	50.6	1.37	1.85	0.24
3**	1.80	125.0	150.6	406.3	111.3	2.70	2.86	0.17

*   Polymer produced by the two-stage method.
** Polymers 2 and 3 were produced by the method of single-stage high-tempera-ture polycyclization in nitrobenzene with initial concentrations of 0.1 and 0.6 m/ℓ respectively.

We studied three unfractionated specimens of polydiphenylenephthalide pyromellitimide which differed in molecular weight and the method of synthesis. The following were determined for all specimens: characteristic viscosity in DMFA, molecular weights by the methods of light scattering and sedimentation in an ultracentrifuge, and coefficients of polydispersity. The methods used for measurement and computation are given in the experimental section. The results show (Table 1) extremely satisfactory agreement between the molecular weights of the polyimides determined by various methods. It is interesting to note that whereas the molecular weight of polyimides synthesized by the two-stage method is not very high ($\overline{M}_w \sim 20,000$, which corresponds to a degree of polymerization P = 40), the polymers resulting from synthesis by single-stage high-temperature polycyclization in solution are characterized by fairly high molecular weights and degrees of polymerization ($\overline{M}_w$ and P for specimen 3 are equal to 125,000 and 250 respectively).

Obviously the data obtained for soluble anilinephthalein polyimides on the principles governing the reaction which produces these polymers and their

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chemical degradation [5,6], on molecular weights and polydispersity, may be applied to other aromatic polyimides as well. In this regard, it is especially important to determine the position occupied by anilinephthalein polypyromellitimide and anilinephthalein imide among other polyimides with respect to the major physicochemical properties, since the thermal stability and heat resistance of aromatic polymers are the very properties which make them so important.

As the data given in Table 2 and Figure 1 show, analinephthalein polypyromellitimides and anilinephthalein imide have exceptionally high thermal stability. In this regard, it should be pointed out that these polymers behave quite differently at high temperatures in air and in an inert atmosphere. Actually, whereas noticeable weight losses in air begin a little above 400°C for anilinephthalein polypyromellitimide, this polymer begins to lose weight in an inert atmosphere only at 460°C. Further evidence that these polyimides are subjected to a thermo-oxidative reaction rather than a purely thermal effect is to be found in the fact that anilinephthalein polypyromellitimide, when heated to 1000°C, burns up completely in air, but when heated to the same temperature in an inert atmosphere, the polymer leaves a residue in the form of a film which has ~60% of the weight of the original specimen (see Fig. 1). Obviously under these conditions the process of carbonization takes place [10] as indicated by the infrared spectrum of the polymer residue when heated to 1000°C, showing none of the bands characteristic of polyimides.


Fig. 1. Thermogravimetric Analysis of Aromatic Polyimides in an inert Atmosphere (He) and in Air at a Rate of Temperature Rise of 5 deg/min on the Electronic Balance made by the Dam Company (France): 1 - 3,3-bis-(4-aminophenyl)phthalide polypyromellitimide; 2 - 9,9-bis-(4-aminophenyl)fluorene polypyromellitimide.

Valuable information on the resistance of polymers to the effect of high temperatures may be derived not only from data of thermogravimetric analysis, but also through measurement of the weight lost by the polymers during protracted isothermal heating. As shown by the data in Table 2, no loss of weight is observed when anilinephthalein polypyromellitimides and anilinephthalein imide are subjected to protracted heating at 300 and 400°C in air. A noticeable loss in weight for these polymers takes place only when they are subjected to protracted heating at 420-430°C.

The effect of the phthalide (phthalimidine) group in anilinephthalein polypyromellitimides and anilinephthalein imides also begins to show up at 420-430°C. The loss in weight (degradation) of anilinephthalein polypyromellitimides at 420-430°C (7%) is chiefly due to the lower thermal stability of the lactone (a) and lactam (b) radicals in the side groups of these polymers as compared with the imide ring, and doesn't involve the principal chain.

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Actually, no weight loss was observed under the conditions given above in the polydiphenylenefluorenepyromellitimide which we synthesized for comparison, a compound which also contains a central carbon atom as part of the cyclic side group (c) in the diamine radical
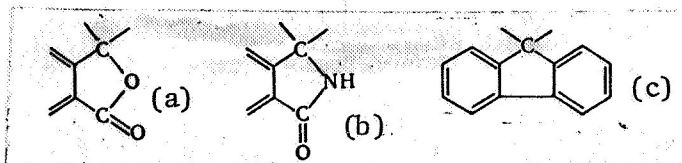
The higher thermal stability of this last polymer as compared with aniline-phthalein polyimides is also indicated by the results of thermographic analysis (see Fig. 1). 9,9-bis-(4-aminophenyl)fluorene polypyromellitimide begins losing weight in air at 460°C, and in an inert atmosphere at >500°C, which is considerably higher than the corresponding values for anilinephthalein polypyromellitimide (410 and 460°C respectively). The residue of 9,9-bis-(4-aminophenyl)fluorene polypyromellitimide after heating to 1000°C in an inert atmosphere has a weight of ~68% of that of the original specimen.

Films based on anilinephthalein polypyromellitimides and anilinephthalein imide are characterized by excellent mechanical indices: the tensile strength at room temperature is 1300-1400 kg/cm^2, and relative longitudinal extension at the breaking point is 30-40%, i.e., in these indices they are as good as polydiphenylene oxide pyromellitimide -- "N film". However, the solubility of anilinephthalein polyimides and anilinephthalein imide makes it possible to pour films from polymers which have already been cyclized.
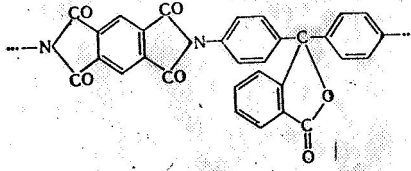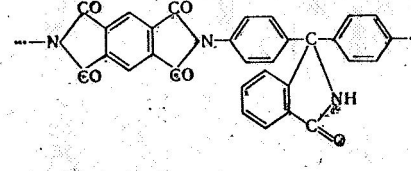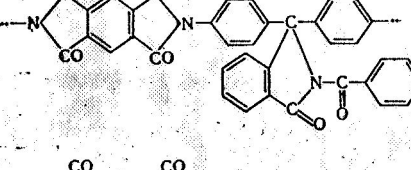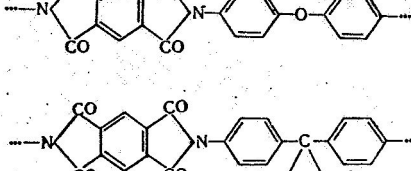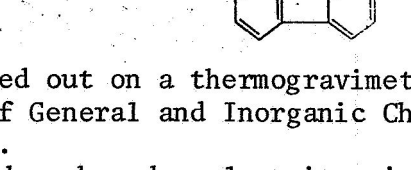
Experimental Section

We outlined the method for synthesizing and purifying anilinephthalein and its imide, as well as pyromellitic dianhydride and the solvents to be used in a previous article [4]. 9,9-bis-(4-aminophenyl)fluorene was synthesized by a method proposed for making 10,10-bis-(4-aminophenyl)anthrone [11]. The diamine was recrystallized several times from ethanol for purification. The melting point of the recrystallized diamine is 236-237°C (233°C according to data in the literature [12].

Synthesis of the polymers. The two-stage method was used for synthesizing polydiphenylenephthalide pyromellitimide by a previously described procedure [4]. The polyimide, synthesized in the form of a film, was purified and homogenized by acetone reprecipitation from a solution in nitrobenzene, thoroughly washed with acetone and ethyl ether, and dried in a vacuum at 80-90°C.

To prepare the polymers by the method of high-temperature polycyclization in solution, a three-necked bottle equipped with an efficient agitator, a diffusor for bubbling inert gas (dry argon) and a drain tube for removing the water formed during the reaction was filled with 6.32 g of anilinephthalein, 4.36g of pyromellitic dianhydride and 190 ml of nitrobenzene. The reaction temperature was gradually raised to 200°C and the reaction mixture was held at this temperature for 10-14 hours. At 180°C, the reaction mixture has already

become homogeneous, which indicates conversion of the amido acid to a soluble polyimide. When the reaction was completed, the reaction mixture was poured into a large excess of acetone. The precipitated polymer was isolated, treated with acetone for extraction, then washed with ethyl ether and dried in a vacuum at 80-90°C. The yield of the polymer is quantative, the $[\eta]$ of the polyimide solution in DMFA at 20°C is 1.02 dl/g.

TABLE 2. RESULTS OF PROTRACTED HEATING OF AROMATIC POLYIMIDES AT HIGH TEMPERATURES IN AIR*

Polyimide structure	Loss in weight**, % 420—430°	
	5 hours	10 hours
	7,10 ***	14,00 ***
	30 ***	—
	41 ****	—
	0 ***	—
	0 ***	—

*   Tests carried out on a thermogravimetric apparatus developed at the Institute of General and Inorganic Chemistry of the Academy of Sciences of the USSR.

**   The polyimides showed no loss in weight after heating at 300°C (25 hours) and 400°C (5 hours).

*** In film.

**** In powder.

Determining the molecular characteristics of the polyimides. The weighted-mean $\overline{M}_w$ and $\overline{M}_z$ -- the average molecular weight of unfractionated poly-pyromellitimide -- was measured by Archibald's method on the G-100 and G-120 ultracentrifuges of the MOM system (Hungary) with a Philpot-Swenson optical system. DMFA was used as the solvent; the cell temperature was 20°C. $\overline{M}_w$ and $\overline{M}_z$ were calculated from data for the meniscus.

The average molecular weights were calculated from the equations

$$\overline{M}_w = \frac{\left(\frac{z}{x}\right)_m \frac{1}{C_m} RT}{\omega^2(1-v\rho)x_m}; \qquad \overline{M}_z = \frac{\frac{\ln z}{x} RT}{x_m \omega^2(1-v\rho)}$$

where z is the ordinate of the gradient curve; x is the distance from the axis of rotation; R is the gas constant; T is absolute temperature; C_m is the concentration of the meniscus solution, equal to

$$C_m = \frac{m_0}{F_1^2 \, \mathrm{tg}\, \theta_1} - \frac{1}{F_2^2 x_m^2 \, \mathrm{tg}\, \theta_2} \sum x^2 z$$

where m is the area under the gradient curve of a separately conducted, so-called refractometric experiment in a two-section cell; F is photographic magnification; θ is the angle of inclination of the slit in the main and refractometric experiments respectively.

Given in Fig. 2 are z/x and log z as functions of x for specimen 3. The /2273 specific partial volume of the polymer (v̄) was calculated from the formula

$$\bar{v} = v_0 \left[\frac{1}{m_0} - \frac{100}{p} \left(\frac{1}{m_0} - \frac{1}{m} \right) \right]$$

where v_0 is the water number of the pycnometer; m_0 is the weight of the solvent in the pycnometer; p is the inverse density of the solution; $p = 100 g v_0/m$, where g is the concentration of the polymer solution and m is the weight of the solution in the pycnometer. For anilinephthalein polypyromellitimide, $\overline{v}$ = = 0.6627. The density of the solvent ρ_{DMFA} = 0.9477, $(1 - \overline{v}\rho)$ = 0.3688.

Svedberg's formula [13] was used for calculating the molecular weight from the rate of sedimentation

$$\overline{M}_w = \frac{S}{D} \frac{RT}{(1-v\rho)}$$

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The sedimentation constant S was determined from the rate of motion of the interface between the pure solvent and the solution (peak of the gradient curve) as a function of the time (t) from the beginning of the experiment at 60,000 rpm and calculation by Svedberg's formula [13].

$$S = \frac{\ln(x_2/x_1)}{\omega^2(t_2 - t_1)}$$

where x_2 and x_1 are the positions of the interface between solution and solvent at times t_2 and t_1; ω is the angular velocity of the ultracentrifuge rotor.
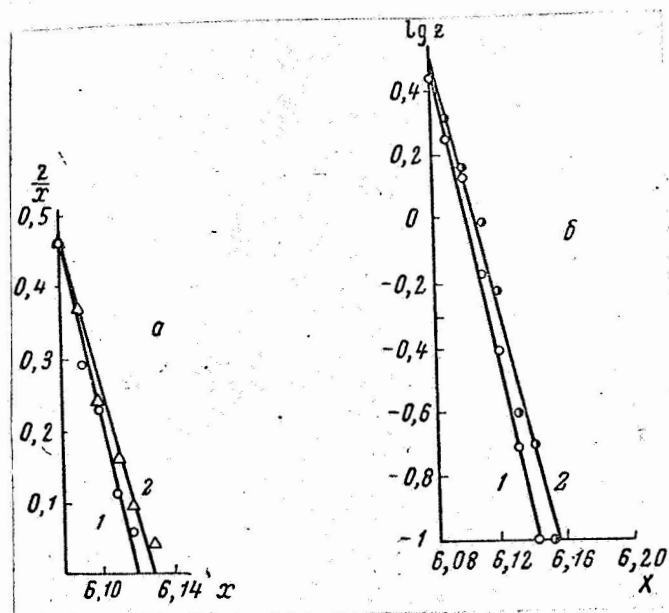

Fig. 2. z/x as a Function of x (a), and log z as a Function of x (b) for Polyimide specimen 3 (see Table 1): 1 - t = = 4200 sec; 2 - t = 6660 sec.

The coefficient of diffusion (D) of anilinephthalein polypyromellitimide was calculated from the second moments of the experimental curves obtained in a two-section cell at 6,000 - 10,000 rpm

$$D = \frac{\overline{\xi_2}^2 - \overline{\xi_1}^2}{2(t_2 - t_1)}$$

The weighted-mean molecular weight $\overline{M}_w$ of unfractionated anilinephthalein polypyromellitimide was measured in DMFA by the method of light scattering on a visual turbidimeter. The measurements of light scattering intensity were made at an angle of 90°. The molecular weight was calculated from the equation

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$$\frac{HC}{R_{90}} = \frac{1}{\overline{M}_w} + \frac{2BC}{RT}$$

where $M = \frac{2\pi^2 n_0^2}{\lambda^4 N_A}\left(\frac{dn}{dc}\right)^2$. R_{90} is the reduced intensity of the scattered light; B is the second virial coefficient; n_0 is the index of refraction of the solvent equal to 1.4269; λ is the wavelength of the incident monochromatic light beam, equal to 5460 Å; N_A is the Avogadro number; dn/dc is the increment in the index of refraction of anilinephthalein polypyromellitimide in DMFA, which is equal

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to 0.231.

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